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ENCAPSULATION OF CHEMILUMINESCENT MATERIALS

by

Leon M. Adams

Chel W. Lew

FINAL REPORT

SwRI Project 01-4248-001

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Prepared for

Dr. George A. Neece

Director, Chemistry Program

Office of Naval Research

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A stable capsule containing Oxalume has been developed using a mixture of paraffin wax and an ethylene-vinyl acetate copolymer as the shell material. Dusting the capsules with either finely powdered sodium acetate or poly (vinyl alcohol) activates the capsules so that the Oxalume will chemiluminesce when the capsules are crushed. The sodium acetate is the more potent activator, but the poly(vinyl alcohol) produces a more stable system.

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A stable capsule containing Oxalume has been developed using a mixture of paraffin wax and an ethylene-vinyl acetate copolymer as the shell material. Dusting the capsules with either finely powdered sodium acetate or poly(vinyl alcohol) activates the capsules so that the Oxalume will chemiluminesce when the capsules are crushed. The sodium acetate is the more potent activator, but the poly(vinyl alcohol) produces a more stable system.

II. INTRODUCTION

Five years ago, Southwest Research Institute developed a stable capsule of TMAE for the Office of Naval Research. This material chemiluminesces on exposure to air, and the shell material, a mixture of calcium alginate and poly(vinyl alcohol), is sufficiently impermeable to oxygen that the encapsulated material is still active after storage in air for five years.

Since the development of TMAE capsules, another chemiluminescent material, Oxalume, which is a more efficient light emitter has been developed and chemiluminesces when it contacts an alkaline surface.

The objective of this research program was to develop stable Oxalume capsules which could be treated in such a way that chemiluminescence would occur on crushing the capsules.

III. EXPERIMENTAL

A. Encapsulation Equipment

In this study, most of the capsules were prepared with the two-orifice centrifugal device with one orifice plugged to aid in determining operating conditions while minimizing requirements of Oxalume. Formation of capsules with this equipment is shown in Figure 1. Figure 2 presents a schematic of this device along with a description of its operation.

The encapsulation head is stainless steel and was passivated prior to use by treatment with 5% nitric acid for 16-20 hours with subsequent rinsing with deionized water and drying. To minimize possible contamination of the Oxalume with metal ions, a plastic syringe pump was utilized for pumping this material through Teflon tubing to the encapsulation head. A Zenith gear pump was used to pump the shell material through 1/4" stainless steel lines to the encapsulating head.

The inner stainless steel orifice (No. 7960 fluid cap) was 20 mils (0.5 mm) in diameter, the outer orifice (No. 7959 air cap) was 40 mils (1 mm) in diameter, and a 15-mil (0.38 mm) spacer was used to separate the fluid and air caps. The assembly is a Spraying Systems Co. air atomizing nozzle, and the numbers in parentheses are part numbers.

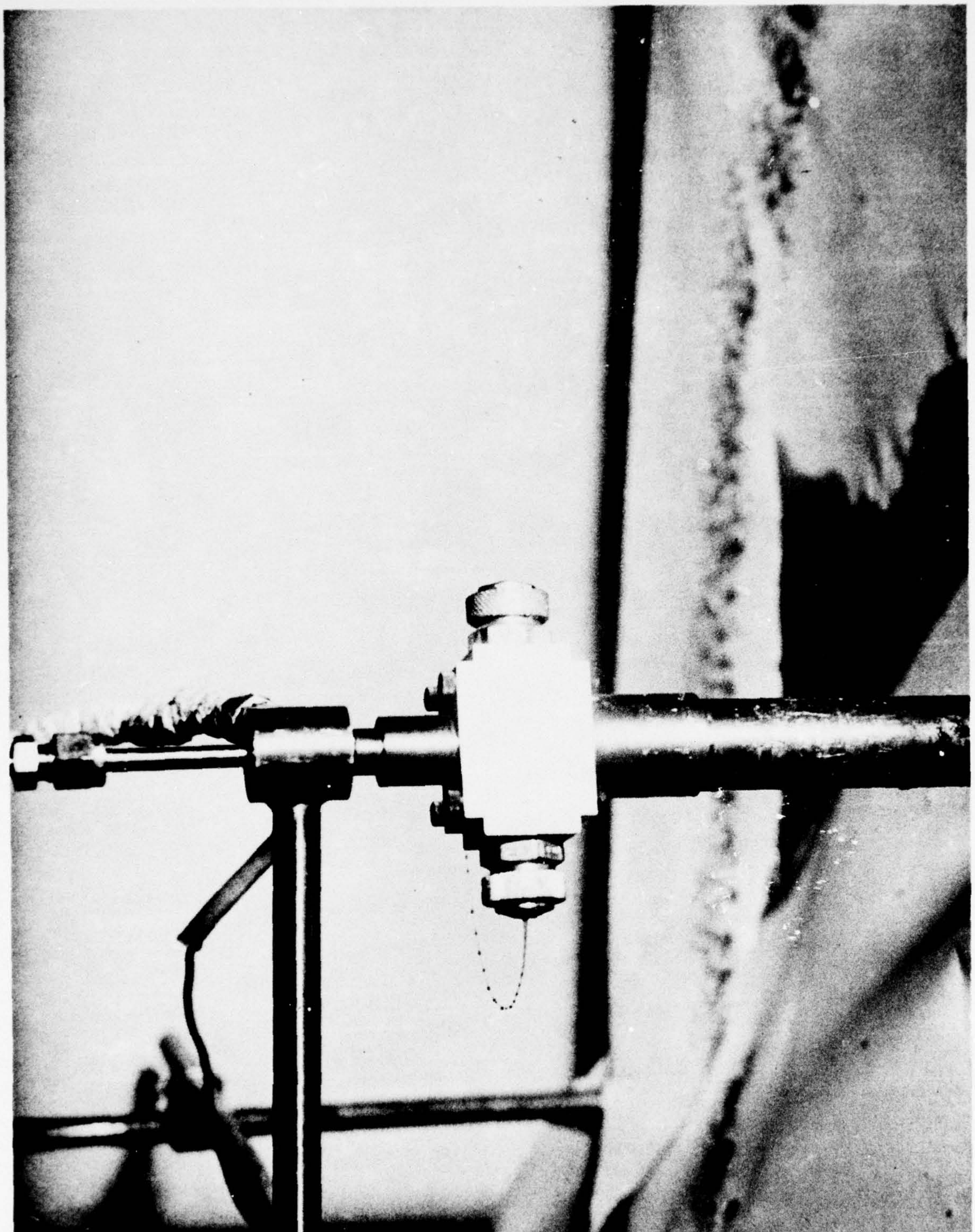

Figure 1.
TWO-ORIFICE CENTRIFUGAL EXTRUSION HEAD
WITH ONE ORIFICE PLUGGED

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CENTRIFUGAL EXTRUSION DEVICE

The centrifugal extrusion device was developed by Southwest Research Institute to provide high production capacity of capsules of uniform quality.

This device, one configuration of which is shown in the schematic drawing, consists of a rotating head which incorporates a plurality of nozzles which are directed radially outward from the axis of rotation. The capsule filler is pumped into the inner chamber and flows through tubes which project into orifices located about the periphery of the head. The fluid shell formulation is pumped into the head and flows through the annuli formed by the orifices and filler tubes. In effect, this results in the extrusion of fluid "rods" of filler encased in sheaths of fluid shell formulation. These "rods" subsequently break into individual fluid capsules, the shells of which are hardened by appropriate means.

This technique of encapsulation offers several advantages over other techniques. In addition to exhibiting a high production rate, the centrifugal extrusion device is capable of handling both fillers and shell formulations of relatively high volatility without loss of vapors. A further advantage lies in the fact that the two streams do not contact one another until the point of encapsulation, and thus, in some cases, it is possible to handle filler and shell formulations which are essentially miscible. Finally, centrifugal force exerted on the extruded materials is utilized to influence capsule size.

A wide range of capsule sizes may be produced with this device, and shell hardening may be accomplished by chemical reaction, solvent extraction, solvent evaporation, cooling, or combination of these techniques.

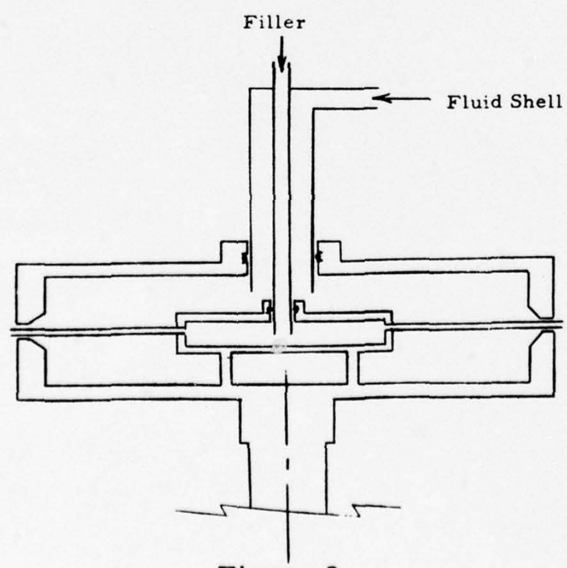

Figure 2.

When only a limited quantity of Oxalume was available, the gravity extrusion device was utilized. Encapsulation with this device is similar to that of the centrifugal device. The orifice is used in a vertical position, and capsules are formed under gravitational force instead of centrifugal force.

B. Aqueous Shell Systems

Aqueous shell systems are normally utilized for encapsulating materials, such as Oxalume, which are insoluble in water. Dibutyl phthalate is the preferred solvent for the preparation of Oxalume, and the initial encapsulation studies were made utilizing this solvent to conserve on Oxalume. Satisfactory capsules (Table 1) were prepared from this material. An alternate solvent (3-methyl-3-pentanol) was also investigated and found difficult to encapsulate in the shell systems evaluated (Table 2).

Capsules prepared from shell systems containing sodium alginate or sodium polypectate are received in a bath containing calcium ions to gel the shells by conversion to the calcium salt. The gelled capsules are then rinsed with deionized water and dried in a fluidized bed dryer using air which is slightly above room temperature. Capsules prepared from shells which do not contain a chemical hardening agent were caught in hydrophobic starch and then dried in the fluidized bed dryer.

TABLE 1. ENCAPSULATION OF DIBUTYL PHTHALATE
(CENTRIFUGAL EXTRUSION DEVICE)

Run No.	Shell Solution, %	Theoretical Payload, %	Size, μ	Comment
1-2A	4.0 Cecalgine TBV sodium alginate 4.0 Elvanol 90-50 PVA 92.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	76	<1190	Capsules made well. No difficulties. 5 percent calcium chloride hardening bath.
1-2B	4.0 Cecalgine TBV sodium alginate 6.0 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	<1190	Capsules made well. No difficulties. 5 percent calcium chloride hardening bath.
1-2C	2.0 Cecalgine TBV sodium alginate 8.0 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	<1190	Capsules made well, but many of the capsules were lost upon drying due to agglomeration. 5 percent calcium chloride hardening bath.
1-2D	4.0 Cecalgine TBV sodium alginate 4.0 Gelvatol 3000 PVA 92.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	76	<1190	Capsules made well. No difficulties. 5 percent calcium chloride hardening bath.
1-2E	4.0 Cecalgine TBV sodium alginate 6.0 Gelvatol 3000 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	<1190	Capsules made well. No difficulties. 5 percent calcium chloride hardening bath.
1-2F	2.0 Cecalgine TBV sodium alginate 8.0 Gelvatol 3000 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	<1190	Capsules made well, but many of the capsules were lost upon drying due to agglomeration. 5 percent calcium chloride hardening bath.

TABLE 2. ENCAPSULATION OF 3-METHYL-3-PENTANOL (CENTRIFUGAL EXTRUSION DEVICE)

Run No.	Shell Solution, %	Theoretical Payload, %	Comment
1-3A	4.0 Cecalgine TBV sodium alginate 4.0 Elvanol 90-50 PVA 92.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	76	Capsules made fairly well, but capsules lost fill on drying. 5-percent calcium chloride bath.
1-3B	4.0 Cecalgine TBV sodium alginate 6.0 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	Capsules made fairly well, but capsules lost fill on drying. 5-percent calcium chloride bath.
1-3C	2.0 Cecalgine TBV sodium alginate 8.0 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	Capsules made fairly well, but capsules lost fill on drying. 5-percent calcium chloride bath.
1-3D	4.0 Cecalgine TBV sodium alginate 4.0 Gelvatol 3000 PVA 92.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	76	No capsules were made. 5-percent calcium chloride bath.
1-3E	4.0 Cecalgine TBV sodium alginate 6.0 Gelvatol 3000 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	No capsules were made. 5-percent calcium chloride bath.
1-3F	2.0 Cecalgine TBV sodium alginate 8.0 Gelvatol 3000 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74	No capsules were made. 5-percent calcium chloride bath.
1-10	4.0 Sodium polypectate 2.0 Gelatin U-Cop-Co 150 Bloom 94.0 Water 0.1 Zonyl FSN surfactant added	80	No capsules were made. 5-percent calcium chloride bath.

Capsules of Oxalume (dibutyl phthalate solvent) were readily prepared (Table 3). Alginate-poly(vinyl alcohol) mixtures were used in run numbers 1-4A and 1-4B, and a mixture of carrageenan and poly(vinyl alcohol) was used as the shell in run number 1-4C. A sodium polypectate-gelatin mixture was utilized in Run No. 1-9. The capsules having alginate in the shell were inactive on drying. Those having polypectate-gelatin shells did not retain the filling. The dried capsules prepared from the carrageenan-poly(vinyl alcohol) mixture glowed brightly in the dark and lost all activity after one day.

A number of potential shell and other materials which would contact the Oxalume during encapsulation were checked for compatibility with Oxalume. The results are presented in Table 4. All of the poly(vinyl alcohol)s were good activators and caused the Oxalume to chemiluminesce. The nonionic surfacts were also activators.

The types of shell materials showing the least amount of activation were investigated further. In some cases, the hardening bath was made acidic, and in other cases, the shell solution was acidified (Tables 5 and 6). None of the capsules remained active after approximately one day. Elimination of the hardening bath by utilizing Dry-Flo (a hydrophobic starch) to collect the capsules, did not produce satisfactory capsules.

Further checks on the effect of activity loss by materials which are known to contact Oxalume or may be present as impurities

TABLE 3. ENCAPSULATION OF OXALUME
(CENTRIFUGAL EXTRUSION DEVICE)

Run No.	Shell Solution, %	Theoretical Payload, %	Size, μ	Comment
1-4A	4.0 Cecalgine TBV sodium alginate 4.0 Elvanol 90-50 PVA 92.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	75.7 (actual)	<1190	Capsules made well. No difficulties. 5-percent calcium chloride hardening bath.
1-4B	3.0 Cecalgine TBV sodium alginate 7.0 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	74.1 (actual)	<1190	Capsules made well. No difficulties. 5-percent calcium chloride hardening bath.
1-4C	1.2 Gelcarin GH carrageenan 8.8 Elvanol 90-50 PVA 90.0 Water 0.1 Tergitol nonionic TMN-6 surfactant added	61.4 (actual)	<1410	Capsules made well. No difficulties. Caught in Dry-Flo, a hydrophobic starch.
1-9	3.0 Sodium polypectate 3.0 Gelatin U-Cop-Co 150 Bloom 94.0 Water 0.1 Zonyl FSN surfactant added	80	–	Capsules made fairly well, but capsules lost fill on drying. 5-percent calcium chloride bath.

TABLE 4. COMPATIBILITY OF VARIOUS MATERIALS WITH OXALUME

Method of Testing: The Oxalume was dropped onto the material being examined in a darkened room.

Materials	Comment
Gelcarin GH carageenan	Some reaction occurred.
Cecalgine TBV sodium alginate	Some reaction occurred.
Elvanol 90-50 poly (vinyl alcohol)	Good activator.
Elvanol 70-05 poly (vinyl alcohol)	Good activator.
Elvanol 71-30 poly (vinyl alcohol)	Good activator.
Gelvatol 20-60 poly (vinyl alcohol)	Good activator.
Gelvatol 3000 poly (vinyl alcohol)	Good activator.
Gelatin U-Cop-Co 150 Bloom	No reaction.
Sodium polypectate	No reaction.
Tergitol nonionic TMN-6 surfactant	Good activator.
Tergitol nonionic TMN-10 surfactant	Good activator.
Triton X-100 nonionic surfactant	Good activator.
Zonyl FSN surfactant	No reaction.
5 percent $CaCl_2$ aqueous solution (tech. grade)	Good activator.
5 percent calcium acetate aqueous solution (CP grade)	No reaction.
Tygon tubing	Very slight reaction occurred.
Silastic tubing	Very slight reaction occurred.
Teflon tubing	No reaction.
Buna N O-ring seals	No reaction.
Silicone O-ring	Very slight reaction.
Fiber gasket (nozzle)	No reaction.
Metal tip of syringe	Very slight reaction.

TABLE 5. ENCAPSULATION OF OXALUME
(CENTRIFUGAL EXTRUSION DEVICE)
(CAPSULE SIZE <1190 MICRONS)

Run No.	Shell Solution, %	Theoretical Payload, %	Comments
1-12	4.0 Celcagine TBV sodium alginate 3.0 U-Cop-Co 150 Bloom type A gelatin 93.0 Water 0.1 Zonyl FSN surfactant added	78.1	Bath–5-percent $CaCl_2$ (pH ~6) with 0.1-percent Zonyl FSN added. Capsules had no activity wet or dry.
1-13	Same	78.1	Bath–10-percent calcium acetate (pH ~ 6) with 0.1-percent Zonyl FSN. Capsules had no activity wet or dry.
1-14A	1.2 Gelcarin GH carrageenan 8.8 Gelatin (Atlantic) type B gelatin 175 Bloom 90.0 Water	76.2	Shell temperature 110°F. Capsules caught in Dry-Flo starch. Capsules had activity for about 2 hours after drying.
1-14B	20.0 U-Cop-Co 300 Bloom type A gelatin 80.0 Water	61.6	Shell temperature 110°F. Capsules caught in Dry-Flo starch. Capsules had no activity wet or dry.
1-14C	4.0 Cecalgine TBV sodium alginate 3.0 Gelatin (Atlantic) 175 Bloom type B 93.0 Water	82.1	Bath–10-percent calcium acetate. Capsules had activity for about two hours after drying.
1-14D	4.0 Cecalgine TBV sodium alginate 3.0 U-Cop-Co 150 Bloom type A gelatin 93.0 Water	82.1	Bath–10-percent calcium acetate. Capsules had no activity wet or dry.
1-14E	1.2 Gelcarin GH carrageenan 8.8 U-Cop-Co 150 Bloom type A gelatin 90.0 Water	–	Shell materials not compatible.
1-15	25.0 Gelatin (Atlantic) 175 Bloom type B 75.0 Water	61.6	Shell temperature 110°F. Capsules in Dry-Flo starch. Capsules glowed in dark when dry and remained active for about 1 day.

TABLE 6. ENCAPSULATION OF OXALUME
(GRAVITY EXTRUSION DEVICE)

Run No.	Shell Solution, %	Comments
1-16A	25.0 Gelatin (175 Bloom, type B) 75.0 Water	Capsules active after 8 hr, but inactive after 24 hr.
1-16B	25.0 Gelatin (175 Bloom, type P) 75.0 Water (Soln. adjusted to pH ~ 5 with HCl)	Some activity after 24 hr. No activity after 48 hr.
1-16C	25.0 Gelatin (150 Bloom, type A) 75.0 Water	No activity after drying.
1-16D	25.0 Gelatin (150 Bloom, type A) 75.0 Water (Soln. adjusted to pH ~ 2 with HCl)	No activity after drying.
1-16E	4.5 Sodium polypectate 95.5 Water	Some activity after 8 hr. No activity after 24 hr. (10-percent calcium acetate bath at pH ~ 4.5)
1-17A	4.5 Sodium polypectate 95.5 Water	Repeat of Run 1-16E with bath at pH ~ 3.0. Re Results same as for 1-16E.
1-17B	25.0 Gelatin (175 Bloom, type B) 75.0 Water (Soln. adjusted to pH ~ 2.0 with HCl)	Similar to Run 1-16B but using lower pH. Activity after 8 hr. No activity after 24 hr.

Note: Gelatin capsules were received on a Dry-Flo starch bed. Fill material was a 50-50 mixture of dibutyl phthalate and Oxalume.

were made by placing some of the material to be investigated in a small polyethylene bottle with Oxalume. The results obtained are presented in Table 7. On examination of the results, it became obvious that water rapidly inactivated the Oxalume. Because of the rapid inactivation of Oxalume by water, no further work was conducted with aqueous systems, and nonaqueous shell systems were investigated.

C. Nonaqueous Shell Systems

The nonaqueous shells investigated were molten mixtures of paraffin waxes and resins. The first encapsulation studies with these mixtures were made with tert-butyl alcohol, 3-methyl-3-pentanol, and dibutyl phthalate (Table 8). Dibutyl phthalate was superior to the two alcohols for forming free-flowing capsules. Table 8 also includes two preliminary runs with Oxalume. It appears that the dibutyl phthalate on hand contained impurities that inactivated Oxalume (Run No. 1-21). Encapsulation of Oxalume in the wax-resin shell appeared promising (Run No. 1-22).

Stability of Oxalume in contact with various shell ingredients was determined (Table 9). Paraffin waxes, ethylene-vinyl acetate copolymers (Elvax), and low molecular weight polyethylenes (AC and Epolene resins) appeared to have little if any effect on Oxalume stability. A terpene polymer (Piccolyte S-115) slowly inactivated the Oxalume. A number of mixtures of candidate shell materials were examined for film formation and flexibility (Table 10). Many of the mixtures appeared

TABLE 7. EFFECT OF CONTAMINANTS ON OXALUME

Contaminant	Comments
None (control)	Good activity after 6 hr.
Ferric chloride (solid)	No activity after 6 hr.
Calcium chloride (solid)	Good activity after 6 hr.
Sodium chloride (solid)	Good activity after 6 hr.
Dry-Flo starch	Good activity after 6 hr.
Cupric sulfate (solid)	Good activity after 6 hr.
Ferrous ammonium sulfate (solid)	Good activity after 6 hr.
Zinc chloride (solid)	No activity after 6 hr.
Glacial acetic acid (one drop in 1 ml)	Slight activity after 6 hr.
Ash from PVA (Elvanol 90-50)	No activity after 6 hr. (glowed immediately).
Sodium chloride (aqueous solution)	Lost activity in 5 min.
Calcium chloride (aqueous solution)	Lost activity in 5 min (glowed immediately).
Cupric chloride (aqueous solution)	Lost activity in 5 min.
Ferrous ammonium sulfate (aqueous solution)	Lost activity in 5 min.
Deionized water	Lost activity in 5 min.

Note: When activity is given after 6 hr, no earlier tests were made.

TABLE 8. ENCAPSULATION RUNS
(CENTRIFUGAL EXTRUSION DEVICE)

Run No.	Shell Composition, %	Fill	Theoretical Payload, %	Size, μ	Comment
1-19A	45.0 Sunoco Wax 4412 45.0 Piccolyte S-115 10.0 Polybutene 128	Tert-butyl alcohol	50.0	–	No capsules.
1-19B	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Elvax 420	Tert-butyl alcohol	50.0	–	No capsules.
1-19C	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Elvax 210	3-Methyl-3-pentanol	50.0	<1190	Made capsules, but capsules leaked on standing.
1-19D	45.0 Sunoco Wax 4412 45.0 Piccolyte S-115 10.0 Polybutene 128	3-Methyl-3-pentanol	50.0	–	No capsules.
1-19E	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Epolene C-16	3-Methyl-3-pentanol	50.0	–	No capsules.
1-19F	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Epolene C-16	50.0-percent 3-Methyl-3-pentanol 50.0-percent Dibutyl phthalate	50.0	–	No capsules.
1-19G	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Elvax 210	Dibutyl phthalate	50.0	<1190	Made capsules well. Capsules remained freeflowing.
1-21	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Elvax 210	50.0-percent Oxalume 50.0-percent Dibutyl phthalate	45.0	<1190	Made capsules well. Lost activity overnight.
1-22	65.0 Sunoco Wax 4412 25.0 Piccolyte S-115 10.0 Elvax 210	Oxalume	45.0	<1190	Made capsules well. Capsules still have activity after a month.

TABLE 9. STABILITY OF CANDIDATE SHELL MATERIALS WITH OXALUME*

Materials Used in Testing	Comments
Control (Oxalume)	Stable after 1 mo.
Sunoco Wax 4412	Stable after 1 mo.
Sunoco Wax 5512	Stable after 1 mo.
Sunoco Wax 3425	Stable after 1 mo.
Shell Wax 100	Stable after 1 mo.
Elvax 210	Stable after 1 mo.
Elvax 220	Stable after 1 mo.
Elvax 240	Stable after 1 mo.
Elvax 310	Stable after 1 mo.
Elvax 350	Stable after 1 mo.
Elvax 410	Stable after 1 mo.
Elvax 420	Stable after 1 mo.
AC-6	Stable after 1 mo.
AC-617	Stable after 1 mo.
Epolene C-16	Stable after 1 mo.
Epolene C-101	Stable after 1 mo.
Piccolyte S-115	Not stable after 1 mo.

*Method of testing: Oxalume placed in polyethylene bottles with the materials being tested. Oxalume used was received on 9/17/76.

TABLE 10. EXAMINATION OF SHELL MATERIALS

Experiment No.	She[redacted], %	Comment
1	80 Sunoco Wax 4412 20 Elvax 210	Film is weak.
2	80 Sunoco Wax 4412 20 Elvax 220	Film is flexible.
3	80 Sunoco Wax 4412 20 Elvax 240	Molten mixture is viscous. Film is flexible.
4	80 Sunoco Wax 4412 20 Elvax 310	Film is flexible.
5	80 Sunoco Wax 4412 20 Elvax 410	Film is flexible.
6	80 Sunoco Wax 4412 20 Elvax 420	Film is flexible and slightly tough.
7	80 Sunoco Wax 5512 20 Elvax 210	Film is flexible.
8	70 Sunoco Wax 5512 30 Elvax 220	Film is flexible and slightly tough.
9	80 Sunoco Wax 5512 20 Elvax 310	Film is flexible.
10	80 Sunoco Wax 5512 20 Elvax 410	Film is flexible.
11	70 Sunoco Wax 5512 30 Elvax 420	Molten mixture is too viscous.
12	70 Sunoco Wax 3425 30 Elvax 210	Molten mixture is too viscous.
13	80 Sunoco Wax 3425 20 Elvax 220	Film is flexible.
14	80 Sunoco Wax 3425 20 Elvax 310	Film is flexible.
15	80 Sunoco Wax 3425 20 Elvax 410	Film is flexible.
16	80 Sunoco Wax 3425 20 Elvax 420	Film is flexible.
17	80 Shell Wax 100 20 Elvax 210	Film is flexible.
18	80 Shell Wax 100 20 Elvax 220	Film is flexible.
19	80 Shell Wax 100 20 Elvax 310	Film is weak.
20	80 Shell Wax 100 20 Elvax 410	Film is flexible.
21	80 Shell Wax 100 20 Elvax 420	Film is flexible.
22	80 Sunoco Wax 4412 20 AC-6	Film is weak.
23	70 Sunoco Wax 4412 30 AC-617	Film is weak.
24	70 Sunoco Wax 4412 30 Epolene C-16	Film is weak.
25	70 Sunoco Wax 4412 30 Epolene C-101	Film is very weak.

TABLE 10. EXAMINATION OF SHELL MATERIALS (Cont'd)

Experiment No.	Shell Mixture, %	Comment
26	70 Sunoco Wax 5512 30 AC-6	Film is very weak.
27	70 Sunoco Wax 5512 30 Epolene C-16	Film is slightly stronger than above.
28	70 Sunoco Wax 3425 30 AC-6	Film is weak and brittle.
29	70 Sunoco Wax 3425 30 Epolene C-16	Film is flexible.
30	70 Shell Wax 100 30 AC-6	Film is weak and brittle.
31	70 Shell Wax 100 30 Epolene C-16	Film is flexible.
32	70 Shell Wax 100 30 Epolene C-101	Film is weak and brittle.
33	70 Sunoco Wax 5512 30 Epolene C-101	Film is weak and brittle.
34	60 Sunoco Wax 4412 40 Epolene C-101	Film is brittle.
35	70 Sunoco Wax 4412 30 Elvax 210	Film is flexible.
36	70 Sunoco Wax 4412 30 Elvax 310	Film is flexible.
37	70 Sunoco Wax 4412 30 Elvax 420	Molten mixture is too viscous.
38	70 Sunoco Wax 5512 30 Elvax 210	Molten mixture is too viscous.
39	70 Sunoco Wax 3425 30 Elvax 420	Molten mixture is too viscous.
40	70 Shell Wax 100 30 Elvax 210	Film is flexible.
41	70 Shell Wax 100 30 Elvax 310	Film is flexible and fairly tough. Viscosity of molten mixture is slightly high.
42	70 Shell Wax 100 30 Elvax 420	Molten mixture is too viscous.
43	70 Sunoco Wax 4412 30 AC-6	Film is brittle.
Method of Testing: Molten mixture shell was spread onto aluminum foil, cooled and examined.		

to be good shell systems, and some of them were evaluated for the encapsulation of dibutyl phthalate (Table 11). Four of the shell systems presented in Table 11 were utilized to make four large samples for evaluation by the Sponsor (Table 12). These samples (each about one pound) were prepared so that long-term aging characteristics of more than one shell system could be determined.

The equipment utilized and operating conditions for the preparation of capsules described in Table 12 are presented in Table 13.

D. Activation of Capsules

Two activators were evaluated. They are sodium acetate and poly(vinyl alcohol), and it is recommended that the capsules be activated just prior to use. A small amount of either activator is dusted onto the capsules. This is readily accomplished by mixing the capsules and activator in a vial or bottle by gentle shaking. Sufficient activator sticks to the capsules to cause the Oxalume to chemiluminesce when the capsules are crushed.

The sodium acetate is a much more potent activator than poly (vinyl alcohol), but the storage life of the activated capsules is much greater when the poly(vinyl alcohol) is used. This is illustrated by the data presented in Table 14.

From the data presented in Table 14, it appears that Sample No. 1-28C produces the most stable activated capsule system. It is believed that the storage stability of the various capsules that are

TABLE 11. ENCAPSULATION OF DIBUTYL PHTHALATE
(THEORETICAL PAYLOAD = 60 wt. % AND SIZE = <1190 MICRONS)

Run No.	Shell Composition, %	Comment
1-25A	80 Sunoco Wax 5512 20 Elvax 220	No capsules were made. Shell mixture too pituitous.
1-25B	80 Sunoco Wax 5512 20 Elvax 420	Capsules had tails.
1-25C	75 Sunoco Wax 3425 25 Elvax 210	Capsules made well.
1-25D	80 Shell Wax 100 20 Elvax 410	Capsules made well.
1-25E	80 Shell Wax 100 20 Elvax 420	Capsules made well, but with some breakage and stringing.
1-25F	75 Sunoco Wax 4412 25 Elvax 210	Capsules made well, but with some breakage and stringing.
1-25G	80 Sunoco Wax 4412 20 Elvax 310	Capsules were made with some stringing.
1-25H	80 Sunoco Wax 4412 20 Elvax 420	No capsules were made. Shell mixture was too pituitous.
1-25I	75 Sunoco Wax 5512 25 Elvax 210	No capsules were made. Shell mixture was too pituitous.
1-25J	80 Sunoco Wax 3425 20 Elvax 420	Capsules made well.
1-25K	70 Shell Wax 100 30 Elvax 210	No capsules were made. Shell mixture was too pituitous.
1-25L	75 Shell Wax 100 25 Elvax 310	Capsules made well. Had some stringing.
1-25M	85 Shell Wax 100 15 Elvax 420	Capsules made well.
1-26A	85 Sunoco Wax 4412 15 Elvax 420	Capsules were made with some breakage and stringing.
1-26B	80 Shell Wax 100 20 Elvax 210	Capsules made well. Stringing occurred when head temperature dropped.
1-26C	85 Sunoco Wax 4412 15 Elvax 310	No capsules. Most capsules broke on collection.
1-26D	70 Sunoco Wax 4412 30 Epolene C-16	Capsules made well.
1-26E	70 Sunoco Wax 5512 30 Epolene C-16	No capsules. Capsules broke on collection.
1-26F	70 Sunoco Wax 3425 30 Epolene C-16	Some capsules were made. Many capsules broke on collection.
1-26G	70 Shell Wax 100 30 Epolene C-16	Capsules made well.
1-26H	60 Sunoco Wax 4412 40 AC-617	No capsules were made.
1-26I	60 Sunoco Wax 3425 40 AC-617	No capsules were made.

TABLE 12. ENCAPSULATION OF OXALUME
(THEORETICAL PAYLOAD = 60 wt. % AND CAPSULE SIZE = < 1190 MICRONS)

Run No. (SwRI No.)	Shell Composition, %	Comment
1-27 (6-929)	75 Sunoco Wax 3425 25 Elvax 210	Capsules made well.
1-28A (6-930)	80 Sunoco Wax 3425 20 Elvax 420	Capsules made well.
1-28B (6-931)	85 Shell Wax 100 15 Elvax 420	Capsules made well.
1-28C (6-932)	70 Shell Wax 100 30 Epolene C-16	Capsules made well.

TABLE 13. ENCAPSULATION EQUIPMENT AND OPERATING CONDITIONS

Orifices:	0.040 inches outside (1 mm) 0.020 inches inside (0.5 mm).
Spacing:	0.015 inches (0.38 mm).
Shell feed rate:	10 g/min.
Fill feed rate:	15 g/min.
Temp Shell feed:	170°F for wax–Elvax. 190°F for polyethylene wax.
Temp Oxalume feed:	Room temperature.
Head temperature:	155°F.
Head speed:	800-900 rpm.

Oxalume feed system was composed of motor-driven polyethylene syringe with teflon tubing to the encapsulation head.

Encapsulation head was stainless steel with teflon bushings and silicone rubber "O" rings. Head was passivated with 5-percent nitric acid overnight, rinsed with deionized water and dried.

The inner orifice is a No. 7960 fluid cap and the outer orifice is a No. 7959 air cap obtained from Spraying Systems Company.

TABLE 14. STABILITY OF CAPSULES COATED WITH ACTIVATOR

Sample No.	Activator*	Initial Activity	Activity after, days				
			2	5	9	20	35
1-27	SA	OK	0	0	0	0	0
1-27	PVOH	OK	OK	OK	Sl	0	0
1-28A	SA	OK	OK	OK	0	0	0
1-28A	PVOH	OK	OK	OK	OK	OK	OK
1-28B	SA	OK	OK	OK	0	0	0
1-28B	PVOH	OK	OK	OK	OK	OK	OK
1-28C	SA	OK	OK	OK	OK	OK	OK
1-28C	PVOH	OK	OK	OK	OK	OK	OK

Test Method

Capsules were placed in a small vial with activator and shaken. Some of the capsules were removed from the mixture at intervals of time and crushed on plain paper in a darkened room to determine activity. The activators were ground to pass a 105-micron screen.

*SA = sodium acetate (<105 micron particles)
PVOH = Elvanol 90-50 (duPont—<105 micron particles)

not activated will be about the same. Oxalume capsules should be stored in a cool room in the absence of light for long shelf life.

IV. CONCLUSIONS

Oxalume is very sensitive to deactivation by water and cannot be encapsulated with aqueous shell systems to produce stable capsules.

Oxalume is not affected appreciably by wax-Elvax or wax-polyethylene mixtures. These mixtures can be utilized to prepare stable Oxalume capsules.

Oxalume capsules can be activated by coating with small amounts of sodium acetate or poly(vinyl alcohol) powder.

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